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Effects of torrefaction and densification on switchgrass pyrolysis products

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HIGHLIGHTS

- The effects of pretreatment on pyrolysis bio-oil components were investigated.
- Torrefaction and densification affected the bio-oil composition.
- Increased torrefaction temperature favored the production of sugars and phenols.
- High pyrolysis temperature favored the production of aromatic compounds.
- Densification favors degradation of cellulose and hemicellulose during pyrolysis.

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ABSTRACT

The pyrolysis behaviors of four types of pretreated switchgrass (torrefied at 230 and 270 °C, densification, and torrefaction at 270 °C followed by densification) were studied at three temperatures (500, 600, 700 °C) using a pyroprobe attached to a gas chromatogram mass spectroscopy (Py-GC/MS). The torrefaction of switchgrass improved its oxygen to carbon ratio and energy content. Contents of anhydrous sugars and phenols in pyrolysis products of torrefied switchgrass were higher than those in pyrolysis products of raw switchgrass. As the torrefaction temperature increased from 230 to 270 °C, the contents of anhydrous sugars and phenols in pyrolysis products increased whereas content of guaiacols decreased. High pyrolysis temperature (600 and 700 °C as compared to 500 °C) enhanced decomposition of lignin and anhydrous sugars, leading to increase in phenols, aromatics and furans. Densification enhanced depolymerization of cellulose and hemicellulose during pyrolysis.

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1. Introduction

Alternative energy sources can play an important role in reducing the dependence on fossil fuels and meeting the future energy demands (Budarin et al., 2009; Thangalazhy-Gopakumar et al., 2011). Biomass has been identified as an alternative, clean and carbon dioxide (CO_2) neutral energy source to produce liquid transportation fuels or biofuels and other forms of energy (Wu et al., 2010). Switchgrass, a perennial, warm-season grass native to the prairies of North America, has emerged as an ideal biomass to produce biofuels because of its high yields of about 15 Mg ha^{-1} (Roth et al., 2005; Sokhansanj et al., 2009), environmental benefits such as a 95% reduction in soil erosion and 90% reduction in pesticide and fertilizer usage and the ability to tolerate diverse growing conditions (Kasi David, 2010). However, similar to other biomass, properties of switchgrass such as low energy and bulk densities, and high moisture content create challenges for storage, transportation and conversion into final fuels, chemicals and power (Karunanithy et al., 2012).

Pretreatments such as torrefaction and densification can be used to improve properties of switchgrass because pretreating biomass results in the breakage of its lignin structure and decomposition of cellulose and hemicellulose structure rendering the biomass more accessible to be pyrolyzed (Srinivasan et al., 2012; Yang et al., 2010). Torrefaction is a thermochemical process which occurs at temperatures between 200 and 300 °C in an inert atmosphere resulting in a hydrophobic product with improved physical and chemical properties and an increased energy density (Tumuluru et al., 2011). Densification increases bulk density of the biomass by converting loose biomass into pellets and briquettes having more uniformity and higher bulk density (Karunanithy et al., 2012; Tumuluru, 2014). A combination of torrefaction and densifi-

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cation may provide additional benefits by increasing both the bulk and energy densities while making biomass hydrophobic.

Biomass is converted into biofuels via two processes namely biochemical and thermochemical conversion processes. Pyrolysis is one of the thermochemical conversion methods to produce liquid fuels and chemicals. In this process biomass is rapidly heated to 450–550 °C in an inert atmosphere with a short residence time resulting in char, vapors and aerosols (bio-oil), and gas (Mohan et al., 2006; Vichaphund et al., 2014). The bio-oil produced is a dark brown liquid and a complex mixture of water (20–25 wt.%) and polar organics (75–80 wt.%) (Bridgwater et al., 1999). Bio-oil can be used in several applications such as boilers, furnaces, turbines and internal combustion engines for heat, power or electricity generation (Czernik and Bridgwater, 2004). However its adverse characteristics such as instability, low heating value, high density, viscosity, acidity, water and oxygen create challenges in its utilization (Budarin et al., 2009; Vichaphund et al., 2014).

Few studies have been performed on pyrolysis of torrefied and densified biomass (De Jong et al., 2003; Meng et al., 2012; Srinivasan et al., 2012). However, there has been no published report on effects of pretreatments on the bio-oil components obtained from pyrolysis of switchgrass. Hence, the objective of this study was to investigate the effects of torrefaction and densification pretreatments and pyrolysis temperatures on the bio-oil components obtained from pyrolysis of switchgrass.

2. Methods

2.1. Biomass characterization

Kanlow switchgrass (*Panicum virgatum*) grown at the Plant and Soil Sciences department at Oklahoma State University was selected as the biomass feedstock. Bales of Kanlow switchgrass were chopped using a Haybuster tub grinder (H1000, Duratech Industries International Inc. Jamestown, N.D) with a screen size of 25 mm. The chopped switchgrass was then ground using a hammer mill (Bliss Industries, Ponca City, Oklahoma) with a mesh size of 4 mm and sent to Idaho National Laboratory (INL, Idaho Falls) for pretreatments. Four types of pretreatment included torrefaction at 230 °C and 270 °C for 30 min residence time, densification, and combined torrefaction and densification (torrefaction at 270 °C for 30 min followed by densification). The mass losses during torrefaction pretreatment at 230 and 270 °C were 25.01 wt.% and 36.70 wt.%, respectively. These losses were attributed to the release of moisture, and condensable and non-condensable volatiles. More details on the operation conditions of pretreatments can be found in our previous study (Sarkar et al., 2014).

Proximate analysis (contents of moisture, volatile, ash and fixed carbon) of biomass sample was determined using a furnace (model 3-550A, Dentsply Prosthetics, PA). The moisture, volatile and ash contents were determined following ASAE standard S358.2 (ASABE Standards, 2006), ASTM D3175 and ASTM E1755-01, respectively. The fixed carbon content was determined by subtracting the volatile and ash contents from the total biomass on dry basis. The ultimate analysis of biomass was measured using an elemental analyzer (PerkinElmer 2400 Series II CHNS/O Elemental Analyzer, Shelton, CT).

The Higher Heating Value (HHV) of biomass was measured using an adiabatic Parr 6200 Bomb Calorimeter (model A1290DDEB, Parr Instrument Co., Moline, Ill). 0.5 g of biomass sample was pelletized using a pellet press and the pellet was kept in a nickel crucible and burned inside a bomb calorimeter surrounded by a water jacket. The sample was ignited by a 10 cm length aluminum wire in presence of oxygen. The wire was placed in such a way that only the tip touched the pellet. Upon ignition, the released heat transferred to the water jacket causing temperature to rise. The increase in temperature was used to calculate HHV of the sample. The HHV measurements were done three times and the average value was reported.

2.2. Py-GC experiments

Pyrolysis experiments were performed in a commercialized pyrolyzer (model No. 5200, CDS Analytics Inc.). The probe had a computer-controlled heating element which held a sample in a quartz tube (25 mm long, 1.9 mm i.d.). Pyrolysis experiments were conducted at three temperatures (500, 600 and 700 °C) at a constant heating rate of 1000 °C/s. About 1 mg of biomass sample was loaded for pyrolysis experiment using helium gas as an inert gas. The volatiles evolved from biomass pyrolysis were carried from the probe into an adsorbent (Tenax-TA™) trap, which was maintained at 40 °C. The condensable bio-oil components were captured by the trap, and the permanent gases were purged out with helium. Then, the bio-oil components were evaporated by heating the trap to 300 °C, and then were directed into a gas chromatography/mass spectrometry (Agilent 7890GC/5975MS) through a heated transfer line for analysis of bio-oil compounds.

The GC column was equipped with a DB-5 capillary column (30 mL $\times$ 0.32 mm i.d., 0.25 μm film thickness). The GC oven temperature was held at 40 °C for 4 min, and then increased at a rate of 5 °C/min to 280 °C and held for 20 min. The injector temperature was 250 °C, and the split ratio was set to 30:1. Helium (purity: 99.99%) was used as a carrier gas at a flow rate of 1 mL/min.

2.3. Experiment design

A full factorial experimental design was used with two factors namely switchgrass pretreatment and pyrolysis temperatures. Five levels of switchgrass pretreatment were (a) no pretreatment (raw switchgrass), (b) torrefaction at 230 °C, (c) torrefaction at 270 °C, (d) densification, (e) combined torrefaction and densification (torrefaction at 270 °C followed by densification). Three levels of pyroprobe (pyrolysis) temperatures were 500, 600 and 700 °C.

3. Results and discussion

3.1. Effects of pretreatment on switchgrass properties

The proximate and ultimate analyses of raw and pretreated switchgrass are shown in Table 1 (Sarkar et al., 2014). It can be seen that moisture contents of switchgrass decreased after pretreatment with torrefaction at 230 and 270 °C. However, moisture content of pellets (switchgrass with densification and combined pretreatments) was not compared with others because pellets were further dried after densification to allow its safe storage. The volatile content decreased after pretreating with torrefaction at 230 °C and continued to decrease as the torrefaction temperature increased to 270 °C due to the partial decomposition of biomass polymers (cellulose, hemicellulose and lignin) and release of light volatiles (Boateng and Mullen, 2013). Densification, on the other hand, did not show significant effect on switchgrass volatile content. However, the combined pretreatment of torrefaction and densification resulted in the least volatile content (62.63 wt.%). Ash content of switchgrass was significantly affected only by the high temperature torrefaction and combined torrefaction and densification pretreatments, which can be due to the high loss of volatiles. Fixed carbon content was significantly affected at all pretreatment conditions except densification. The fixed carbon content of switchgrass pretreated with combined torrefaction and densification was the highest (31.45 wt.%) followed by those

Table 1
Proximate and ultimate analysis and HHV of pretreated switchgrass. Adapted from Sarkar et al., 2014.

	Raw SG	T230	T270	DEN	T270 + DEN
Proximate analysis (w.b. wt.%)					
Moisture content	9.80 ± 0.65*	2.39 ± 0.61	2.05 ± 1.04	5.05 ± 0.78	7.44 ± 0.15
Volatile matter	80.63 ± 0.18	78.99 ± 0.54	67.52 ± 0.93	80.23 ± 0.54	62.63 ± 0.23
Ash content	3.50 ± 0.44	3.63 ± 0.15	4.98 ± 0.50	3.62 ± 0.14	5.91 ± 0.16
Fixed carbon	15.87 ± 0.42	17.38 ± 0.45	27.51 ± 1.38	16.15 ± 0.67	31.45 ± 0.38
Ultimate analysis (d.b. wt.%)					
Carbon	47.37 ± 0.03	52.79 ± 0.16	59.16 ± 0.45	47.11 ± 0.29	52.09 ± 0.34
Hydrogen	6.61 ± 0.18	5.77 ± 0.27	4.67 ± 0.28	5.93 ± 0.12	5.13 ± 0.11
Oxygen	43.97 ± 0.35	39.58 ± 0.59	34.53 ± 1.00	45.44 ± 0.37	41.34 ± 0.15
Nitrogen	0.62 ± 0.01	0.32 ± 0.08	0.44 ± 0.18	0.29 ± 0.01	0.39 ± 0.01
Sulfur	1.43 ± 0.13	1.54 ± 0.08	1.20 ± 0.08	1.24 ± 0.04	1.05 ± 0.06
HHV (MJ/kg)	20.60 ± 0.69	23.53 ± 0.19	27.11 ± 0.27	19.14 ± 0.25	22.27 ± 0.32

SG = switchgrass, T230 = switchgrass torrefied at 230 °C, T270 = switchgrass torrefied at 270 °C, DEN = densified switchgrass, T270 + DEN = switchgrass pretreated by combined torrefaction and densification.

[*] Values listed above are means ± standard deviation of three samples.

of switchgrass pretreated with torrefaction at 270 and 230 °C. The ultimate analysis indicated that the carbon content increased significantly with torrefaction and combined pretreatments of torrefaction and densification. In addition, the carbon content increased significantly as the torrefaction temperature increased from 230 to 270 °C. An inverse trend was observed for both hydrogen and oxygen contents. Densification had no significant effects on carbon and oxygen contents according to Duncan multiple range tests. The HHV of switchgrass increased with all pretreatment conditions except densification. As shown in the Van Krevelen diagram (Sarkar et al., 2014), the increase in HHV could be due to a decrease in oxygen to carbon (O/C) and hydrogen to carbon (H/C) ratios of the switchgrass when pretreated with torrefaction.

3.2. Characterization of pyrolysis products

The chemical compositions of pyrolysis products of raw and pretreated switchgrass obtained at three temperatures (500, 600 and 700 °C) are classified into different families as shown in Figs. 1–3. More than 100 compounds were identified by comparing the spectrum with the MS library. The pyrolysis products can be classified into various families according to their functional groups, such as ketones, anhydrous sugars, furans, phenols, guaiacols, syringols, aromatics and carboxylic acids. Similar observations have been reported earlier (Meng et al., 2012; Thangalazhy-Gopakumar et al., 2011). Among these groups, ketones, anhydrous sugars, furans and carboxylic acids are derived from decomposition of cellulose and hemicellulose, and the remaining groups are derived from decomposition of lignin derived oligomers. Tables 2–4 list the major compounds (with relative peak area >=1%) and their relative area percentages obtained from the pyrolysis of all samples obtained at 500, 600 and 700 °C, respectively. All the listed chemical compounds were sorted according to chemical families and sources. It can be seen that majority of the compounds are oxygenated polar species. Although most of the compounds in

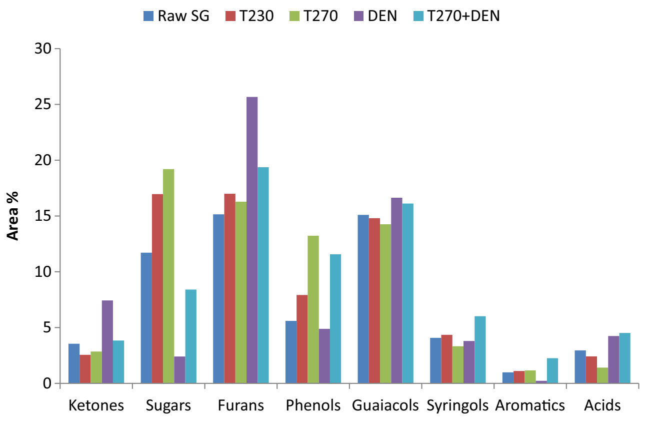

Fig. 1. Product distribution of raw and pretreated switchgrass pyrolyzed at 500 °C (SG = switchgrass, T230 = switchgrass torrefied at 230 °C, T270 = switchgrass torrefied at 270 °C, DEN = densified switchgrass, T270 + DEN = switchgrass pretreated by combined torrefaction and densification).

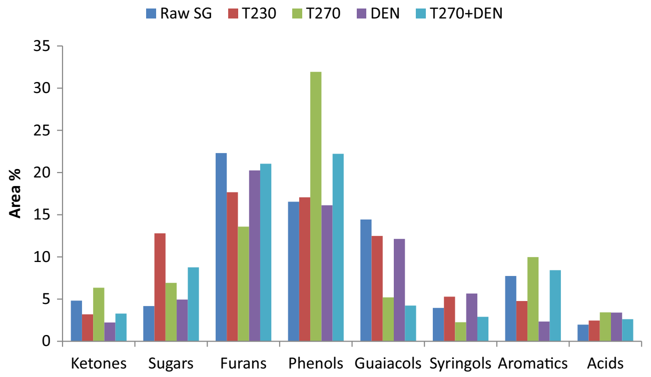

Fig. 2. Product distribution of raw and pretreated switchgrass pyrolyzed at 600 °C. (SG = switchgrass, T230 = switchgrass torrefied at 230 °C, T270 = switchgrass torrefied at 270 °C, DEN = densified switchgrass, T270 + DEN = switchgrass pretreated by combined torrefaction and densification).

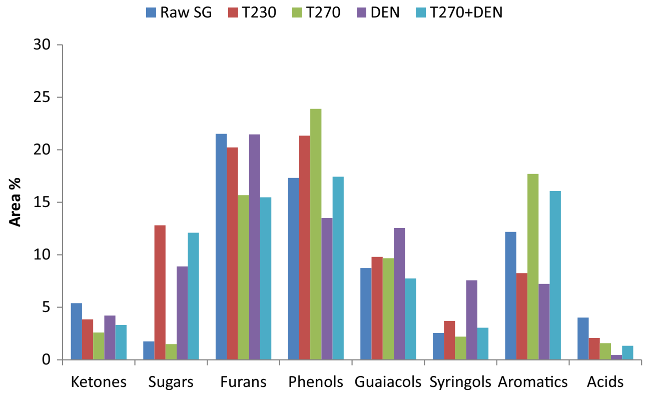

Fig. 3. Product distribution of raw and pretreated switchgrass pyrolyzed at 700 °C. (SG = switchgrass, T230 = switchgrass torrefied at 230 °C, T270 = switchgrass torrefied at 270 °C, DEN = densified switchgrass, T270 + DEN = switchgrass pretreated by combined torrefaction and densification).

Table 2
Pyrolysis products of raw and torrefied switchgrass obtained at 500 °C[a].

Chemicals	Group	Raw SG	T230	T270	DEN	T270 + DEN
Cellulose/hemicellulose derived compounds (area%)						
Benzofuran, 2,3-dihydro-	Furans	6.36	4.14	2.30	9.45	4.14
Furfural	Furans	3.08	2.25	1.78	4.25	–
Furan, 2-methyl-	Furans	1.44	1.65	1.63	3.09	2.49
2-Furancarboxaldehyde, 5-methyl-	Furans	1.28	1.35	1.53	1.31	2.02
2(3H)-Furanone, 5-methyl-	Furans	–	2.08	1.87	–	1.85
5-Hydroxymethylfurfural	Furans	–	1.18	1.07	1.02	–
Acetic acid	Acid	2.95	1.40	–	4.24	1.66
3,4-Altrosan	Sugars	3.08	3.42	–	–	–
.beta.-D-Glucopyranose, 1,6-anhydro-	Sugars	5.96	7.27	13.36	–	5.90
D-Allose	Sugars	2.40	5.15	5.14	–	1.66
1,2-Cyclopentanedione	Ketones	2.07	–	–	1.46	–
1,2-Cyclopentanedione, 3-methyl-	Ketones	1.12	–	1.53	–	–
2-Cyclopenten-1-one, 2-hydroxy-3-methyl-	Ketones	–	1.26	–	1.77	1.76
Lignin derived compounds (area%)						
Phenol	Phenols	–	1.17	1.61	–	1.64
p-Cresol	Phenols	1.02	1.47	2.31	–	2.18
Catechol	Phenols	1.55	1.89	3.00	1.62	2.58
Phenol, 4-ethyl-	Phenols	–	–	1.04	–	1.21
2-Methoxy-4-vinylphenol	Guaiacols	5.79	4.22	2.66	7.00	4.14
1,2-Benzenediol, 3-methoxy-	Guaiacols	–	–	1.73	–	1.64
Phenol, 4-ethyl-2-methoxy-	Guaiacols	–	–	1.77	–	1.70
Creosol	Guaiacols	2.11	–	3.87	2.24	3.26
Phenol, 2-methoxy-	Guaiacols	1.98	2.19	–	1.89	2.30
Benzoic acid, 4-hydroxy-3-methoxy-	Guaiacols	1.76	–	1.85	–	1.08
3,5,-dimethoxyacetophenone	Syringols	2.44	–	–	1.27	1.51
Phenol, 2,6-dimethoxy-4-(2-propenyl)-	Syringols	1.32	1.25	–	1.46	1.63
Phenol, 2,6-dimethoxy-	Syringols	1.55	2.56	2.19	2.08	2.53
Toluene	Aromatics	–	1.10	1.16	1.45	1.50

SG = switchgrass, T230 = switchgrass torrefied at 230 °C, T270 = switchgrass torrefied at 270 °C, DEN = densified switchgrass, T270 + DEN = switchgrass pretreated by combined torrefaction and densification.

[a] "–" means the peak area percentage of the detected compound is less than 1%.

pyrolysis products obtained from both raw and pretreated switchgrass were similar, their quantity (and hence yield) differed.

3.2.1. Effects of torrefaction

Significant compositional variation can be found between the pyrolysis products of raw and torrefied switchgrass. As shown in Fig. 1, anhydrous sugars, furans, phenols and guaiacols are the four most abundant groups identified in the pyrolysis product of both raw and torrefied switchgrass. At 500 °C pyrolysis temperature, anhydrous sugar content increased with torrefaction and increase in torrefaction temperature. Anhydrous sugar contents obtained were 11.71, 16.96 and 19.19 area% from raw switchgrass, switchgrass torrefied at 230 °C and switchgrass torrefied at 270 °C, respectively. However, increase in the anhydrous sugars content due to torrefaction was not consistent when pyrolysis temperature increased to 600 and 700 °C, as shown in Figs. 2 and 3. One of the major anhydrous sugars listed in Table 2 (at pyrolysis temperature of 500 °C), was 6-anhydro-β-D-Glucopyranose (also known as levoglucosan). Levoglucosan was found to increase from 5.96 area% obtained from raw switchgrass to 7.27 area% obtained from switchgrass torrefied at 230 °C, and then to 13.36 area% obtained from switchgrass torrefied at 270 °C. The furans content increased slightly from 15.14 area% obtained from raw switchgrass to 16.99 area% obtained from switchgrass torrefied at 230 °C, however, no significant variation was observed in furans content obtained from switchgrass torrefied at 270 °C and 230 °C. Among the furans listed in Table 2, both 2,3-dihydro-benzofuran and furfural decreased drastically after torrefaction, and further decreased with increase in torrefaction temperature from 230 to 270 °C. However, no consistent trend was observed for other furans identified as the major compounds. Few earlier studies on pyrolysis of torrefied biomass reported that furans content decreased with torrefaction pretreatment when pyrolysis temperature ranged from 480 to 650 °C (Meng et al., 2012; Ren et al., 2013; Srinivasan et al., 2012). Interestingly, in this study, the decreasing trend of furans with torrefaction was noticeable when pyrolysis temperature increased to 600 and 700 °C, as shown in Figs. 2 and 3.

As for lignin-derived compounds, at 500 °C pyrolysis temperature, the phenols in pyrolysis products of switchgrass torrefied at 230 and 270 °C were 7.92 and 13.23 area%, respectively, which were significantly higher than that in pyrolysis products of raw switchgrass (5.59 area%). Similar increasing trend of phenols was also noticeable at pyrolysis temperature of 600 and 700 °C, as shown in Figs. 2 and 3. Consistently, significant increasing trend of typical phenol compounds (listed in Table 2) i.e. phenols, p-cresol and catechol was observed. Guaiacols, the main oxygenates derived from lignin oligomers slightly decreased on torrefaction (14.80 area% obtained from switchgrass torrefied at 230 °C to 15.10 area% obtained from raw switchgrass). 2-Methoxy-4-vinylphenol, one of the dominant guaiacols, decreased significantly from 5.79 area% obtained from raw switchgrass to 2.66 area% obtained from switchgrass torrefied at 270 °C. The guaiacols content decreased significantly as the severity of torrefaction increased at 600 °C pyrolysis temperature, i.e. the total area% of guaiacols obtained from raw switchgrass and switchgrass torrefied at 270 °C were 14.43 to 5.20, respectively. However, at 700 °C pyrolysis temperature, guaiacols content increased slightly from 8.73 area% obtained from raw switchgrass to 9.80 area% obtained from switchgrass torrefied at 230 °C, but no significant change was observed between guaiacols obtained from switchgrass torrefied at 230 and 270 °C.

The above analysis of pyrolysis products obtained from raw and torrefied switchgrass indicate that torrefaction promotes the production of anhydrous sugars and phenols. Hence, torrefaction can promote pyrolysis-based biorefinery by producing multiple high-value chemicals in only few conversion steps. Toluene was the only

Table 3
Pyrolysis products of raw and torrefied switchgrass obtained at 600 °C[a].

Chemicals	Group	Raw SG	T230	T270	DEN	T270 + DEN
Cellulose/Hemicellulose derived compounds (area%)						
Benzofuran, 2,3-dihydro-	Furans	9.33	5.80	2.99	9.11	5.085
Furfural	Furans	4.84	2.96	1.78	3.24	2.88
Furan, 2-methyl-	Furans	–	2.86	–	–	2.15
2-Furancarboxaldehyde, 5-methyl-	Furans	1.94	1.55	1.84	1.42	2.49
2(3H)-Furanone, 5-methyl-	Furans	1.44	1.97	–	2.35	2.54
5-Hydroxymethylfurfural	Furans	–	1.34	1.23	1.21	1.32
2-Furanmethanol	Furans	1.20	1.10	1.04	1.22	1.27
2(5H)-Furanone	Furans	1.59	1.10	–	–	1.13
Acetic acid	Acid	1.49	2.09	–	3.40	1.42
3,4-Altrosan	Sugars	1.13	1.64	–	–	–
.beta.-D-Glucopyranose, 1,6-anhydro-	Sugars	2.38	4.93	–	4.40	–
D-Allose	Sugars	–	5.59	3.74	–	1.11
2-Cyclopenten-1-one, 2-hydroxy-3-methyl-	Ketones	1.33	1.61	1.93	1.38	1.91
Lignin derived compounds (area%)						
Phenol	Phenols	1.47	2.33	3.20	1.62	3.69
p-Cresol	Phenols	2.22	–	5.10	–	4.13
Catechol	Phenols	3.08	3.70	5.49	3.08	5.22
4-Ethylcatechol	Phenols	–	–	1.26	–	1.15
Phenol, 2-methyl-	Phenols	1.03	–	2.22	–	2.18
Phenol, 4-ethyl-	Phenols	1.27	1.35	1.95	1.03	1.76
1,2-Benzenediol, 3-methyl-	Phenols	1.51	–	2.50	1.72	2.01
1,2-Benzenediol, 4-methyl-	Phenols	1.68	2.07	3.81	2.04	2.82
2-Methoxy-4-vinylphenol	Guaiacols	6.46	4.52	1.75	5.95	2.43
Creosol	Guaiacols	2.29	2.17	1.11	1.69	1.02
Phenol, 2-methoxy-	Guaiacols	1.44	1.51	1.33	1.30	1.12
Phenol, 2,6-dimethoxy-4-(2-propenyl)-	Syringols	1.29	–	–	1.29	–
Phenol, 2,6-dimethoxy-	Syringols	1.82	1.95	1.67	1.78	1.66
Toluene	Aromatics	2.11	2.15	2.63	2.09	2.97
Benzene	Aromatics	3.87	–	1.43	–	1.27
p/o-Xylene	Aromatics	–	1.02	–	–	1.31
Benzene, 1,3-dimethyl-	Aromatics	1.00	–	1.44	–	–

SG = switchgrass, T230 = switchgrass torrefied at 230 °C, T270 = switchgrass torrefied at 270 °C, DEN = densified switchgrass, T270 + DEN = switchgrass pretreated by combined torrefaction and densification.

[a] "–" means the relative peak area percentage of the detected compound is less than 1%.

aromatic compound identified in the pyrolysis products of both raw and torrefied switchgrass at 500 °C with small increase in the toluene content after torrefaction. Similar results were reported in the literature (Thangalazhy-Gopakumar et al., 2011). Aromatics larger than toluene could have condensed in the trap or be in low concentration. Other simple oxygenates such as ketones and carboxylic acids were also detectable. Ketones were dominated by cycloketones with five carbon rings that are derived from depolymerization of levoglucosan or conversion of 5-hydroxymethylfurfural (Thangalazhy-Gopakumar et al., 2011). Acetic acid was the primary carboxylic acid in pyrolysis products of raw and torrefied switchgrass, the content of which decreased from 2.95 to less than 1 area% after torrefaction at 270 °C. This finding is consistent with results reported in the literature (Meng et al., 2012; Ren et al., 2013).

The variation in the composition of pyrolysis product obtained from raw and torrefied switchgrass was due to partial decomposition of cellulose and hemicellulose during torrefaction (Meng et al., 2012). Thermal stability, decomposition rates and decomposition products of the three biomass components (cellulose, hemicellulose and lignin) differ. Hemicellulose is considered as the most thermally unstable component that decomposes mainly at 220–315 °C, whereas lignin is the most stable one that degrades at a broader temperature range of 160–900 °C (Pasangulapati et al., 2012; Yang et al., 2007). In addition, the pyrolysis products from these three components are also very different. The pyrolysis of hemicellulose mainly produces small molecules such as ketones, acetic acid and furfural. Cellulose is the dominant source for the production of anhydrous sugars and furans. Lignin produces most of the phenols and phenol derivatives. Researchers have also found strong interaction effects of hemicellulos-cellulose and cellulose–lignin during pyrolysis (Hosoya et al., 2007; Wang et al., 2011). They hypothesized that hemicellulose decomposes prior to cellulose and forms a liquid film wrapping around the surface of cellulose thereby inhibiting the decomposition of cellulose, thus leading to a decrease in anhydrous sugars production. Another theory is that cellulose-derived volatiles act as H-donors that stabilize the lignin derived compounds (e.g. guaiacols and syringols acting as H-acceptors) via O-CH_3 homolysis to produce phenols and methane (Hosoya et al., 2009). The interaction of hemicellulose–cellulose could be mitigated or eliminated, and the interaction of cellulose–lignin could be promoted by torrefaction pretreatment because torrefaction removes most hemicellulose from the raw biomass (Zheng et al., 2012) and concentrates cellulose and lignin as a result. This may explain the increase of anhydrous sugars and phenols in the pyrolysis product of switchgrass pretreated by torrefaction. Previous studies (Boateng and Mullen, 2013; Zheng et al., 2012) have shown that hemicellulose and cellulose derived compounds, such as acetic acids, hydroxyl ketones, furans and levoglucosan are the dominant while lignin derived compounds such as phenols, guaiacol and vanillin were negligible in the volatile products of biomass torrefaction. Our finding further confirmed that chemical transformation during torrefaction process affects composition of pyrolysis products obtained from the torrefied biomass.

3.2.2. Effects of pyrolysis temperature

The composition of pyrolysis products obtained from both raw and torrefied switchgrass at elevated temperature (600 and 700 °C) were different from those obtained at pyrolysis temperature of 500 °C. The four most abundant groups (anhydrous sugars, furans,

Table 4
Pyrolysis products of raw and torrefied switchgrass obtained at 700 °C[a].

Chemicals	Group	Raw SG	T230	T270	DEN	T270 + DEN
Cellulose/hemicellulose derived compounds (area%)						
Benzofuran, 2,3-dihydro-	Furans	10.71	6.30	3.13	9.69	3.81
Furfural	Furans	3.82	2.94	–	3.17	–
Furan, 2-methyl-	Furans	–	–	2.80	–	2.41
Furan, 2,5-dimethyl-	Furans	–	–	2.23	–	2.12
2-Furancarboxaldehyde, 5-methyl-	Furans	1.71	1.63	1.06	1.17	1.61
2(3H)-Furanone, 5-methyl-	Furans	–	2.46	1.78	1.59	–
5-Hydroxymethylfurfural	Furans	–	1.39	1.21	–	–
2-Furanmethanol	Furans	–	1.22	–	1.33	–
Acetic acid	Acid	4.01	2.07	1.58	–	1.33
D-Allose	Sugars	–	5.78	–	2.82	3.61
.beta.-D-Glucopyranose, 1,6-anhydro-	Sugars	1.05	6.62	–	4.94	3.55
2-Cyclopenten-1-one, 2-hydroxy-3-methyl-	Ketones	1.08	–	1.30	1.13	1.00
1,2-Cyclopentanedione	Ketones	1.97	1.36	–	–	1.69
Lignin derived compounds (area%)						
Phenol	Phenols	2.99	2.83	5.01	2.03	3.52
p-Cresol	Phenols	2.95	–	–	–	3.72
Catechol	Phenols	3.90	4.44	3.20	2.80	2.58
Phenol, 2-methyl-	Phenols	1.24	1.02	2.05	2.01	1.43
Phenol, 4-ethyl-	Phenols	1.44	1.46	1.40	–	1.10
Phenol, 2,4-dimethyl-	Phenols	1.19	1.17	1.72	–	1.40
1,2-Benzenediol, 3-methyl-	Phenols	1.64	1.89	–	–	–
1,2-Benzenediol, 4-methyl-	Phenols	2.29	2.76	1.39	1.50	–
2-Methoxy-4-vinylphenol	Guaiacols	4.45	3.79	2.25	6.37	2.35
Creosol	Guaiacols	–	2.57	1.89	1.81	1.08
Phenol, 2-methoxy-	Guaiacols	–	1.47	1.78	1.44	1.28
Phenol, 2,6-dimethoxy-	Syringols	1.37	2.07	1.72	2.04	1.18
Toluene	Aromatics	3.80	3.15	4.30	2.97	3.86
Benzene	Aromatics	2.55	1.61	3.49	–	3.07
Xylene	Aromatics	1.24	1.16	1.42	–	–
Styrene	Aromatics	1.28	–	1.78	–	1.22

SG = switchgrass, T230 = switchgrass torrefied at 230 °C, T270 = switchgrass torrefied at 270 °C, DEN = densified switchgrass, T270 + DEN = switchgrass pretreated by combined torrefaction and densification.

[a] "–" means the relative peak area percentage of the detected compound is less than 1%.

phenols and guaiacols) obtained at 500 °C pyrolysis were still dominant in the pyrolysis products at 600 and 700 °C. However, the content of aromatic compounds obtained at 500 °C pyrolysis temperature was lower than that obtained at the elevated pyrolysis temperatures (600 and 700 °C). As shown in Fig. 2, the aromatics contents obtained from raw switchgrass, switchgrass torrefied at 230 and 270 °C were 7.74, 4.77 and 9.98 area%, respectively at 600 °C, and then increased to 12.18 and 8.25 area% at 700 °C, respectively. In addition, aromatics other than toluene such as benzene, xylenes, and styrene were also detected (as shown in Tables 3 and 4). Other polymeric aromatic compounds, such as naphthalene were also detected but in low concentration. The aromatics were mainly derived from decomposition of lignin-derived oligomers such as guaiacols and syringols (Thangalazhy-Gopakumar et al., 2011), and the decomposition rate increases with increase in pyrolysis temperature. The guaiacols content obtained from raw switchgrass, switchgrass torrefied at 230 and 270 °C decreased from 15.10, 14.80, and 14.25 area%, respectively, at 500 °C to 14.43, 12.48 and 5.20 area%, respectively, at 600 °C, and further decreased to 8.73 and 9.80 area%, respectively, at 700 °C. Similar decreasing trend was also observed for syringols. On the contrary, the phenols in switchgrass pyrolysis products of raw and torrefied at 230 °C increased from 5.59 and 7.92 area%, respectively, at 500 °C to 16.54 and 17.06 area%, respectively, at 600 °C and further increased to 17.32 and 21.34 area%, respectively, at 700 °C, respectively. The conversion pathways of lignin pyrolysis involve three processes (Mullen and Boateng, 2010; Srinivasan et al., 2012): depolymerization of lignin, conversion of lignin monomers into guaiacols or syringols, and conversion of guaiacols or syringols into simple phenols and aromatic compounds (see Supplementary material, Fig. S1). Phenols are derived from either depolymerization of lignin or decomposition of lignin oligomers such as guaiacols (Mullen and Boateng, 2010), and these reactions are highly enhanced at elevated temperature. This may explain the increase of phenol compounds in the pyrolysis products when pyrolysis temperature was increased.

The contents of anhydrous sugars in pyrolysis products of raw switchgrass, switchgrass torrefied at 230 and 270 °C obtained at 600 °C and 700 °C were significantly lower as compared to those obtained at 500 °C. In detail, the content of dominant anhydrous sugar compound, levoglucosan, obtained from pyrolysis of raw switchgrass dropped from 5.96 at 500 °C to 2.38 at 600 °C and then to 1.05 area% at 700 °C. On the contrary, furans, increased with increase in pyrolysis temperature. This was also noticeable when comparing content of a typical furan compound, such as 1,3-dihydro-benzofuran. Based on numerous investigation on the mechanism of cellulose pyrolysis (Antal and Varhegyi, 1995; Boutin et al., 1998; Demirbaş, 2000; Shafizadeh, 1982; Shen et al., 2010), cellulose first decomposes into oligosaccharides, known as active cellulose and then further degrades into anhydrous monosaccharides such as levoglucosan and D-Allose, and these monosaccharides can further transform by dehydration, decarboxylation or decarbonylation to form furans or fragment to form simpler linear carbonyl compound such as hydroxyacetaldehyde. Levoglucosan is considered an important pyrolytic product that can either be utilized in organic synthesis or hydrolyzed into glucose for bioethanol production (Zhu and Lu, 2010). The maximum yield of levoglucosan reported in the literature was 40 wt.% using pure cellulose as the substrate (Piskorz et al., 1989), however, yield from pyrolysis of lignocellulosic biomass is expected to be much lower due to the catalytic effect of inorganic metals (Zhu and Lu, 2010).

3.2.3. Effect of densification

By comparing compositions of pyrolysis products obtained from raw switchgrass, densified switchgrass, switchgrass torrefied at 270 °C and switchgrass pretreated by combined torrefaction and densification at 500 °C pyrolysis, it can be seen that the yield of anhydrous sugars decreased significantly due to densification, i.e. the anhydrous sugars obtained from densified switchgrass (2.41 area%) were much lower as compared to those obtained from raw switchgrass (11.71 are%). However, the sugar content obtained from densified switchgrass at 600 and 700 °C were higher pyrolysis temperatures compared to that at 500 °C. On the other hand, furans content obtained from densified (25.66 area%) and torrefied-densified switchgrass (19.37 area%) were higher compared to those obtained from non-densified switchgrass. It should also be noticed that acetic acid content obtained from densified and torrefied-densified switchgrass were 4.24 and 4.51 area%, respectively that were 1.5 and 2-folds higher than that obtained from non-densified switchgrass. In addition, cycloketones content also increased significantly due to densification. These results indicate that densification promoted the depolymerization of hemicellulose and cellulose resulting in production of furans, cycloketones and ring-scission products such as acetic acids. Densification also mildly promoted production of lignin-derived compounds such as guaiacols and lowered yield of phenols. As can be observed from Fig. 1, phenols content obtained from densified and torrefied-densified switchgrass dropped to 4.88 and 11.56 area%, respectively, compared to those obtained from raw switchgrass (5.59 area%) and switchgrass torrefied at 270 °C (13.23 area%). The guaiacols contents obtained from densified (16.63 area%) and torrefied-densified (16.11 area%) switchgrass were higher as compared to that obtained from non-densified switchgrass. Proximate and ultimate analyses of densified switchgrass were not significantly different from those of raw switchgrass. These results are comparable to Rijal et al. (2012) who concluded that the densification process had no significant impact on the chemical composition (cellulose, hemicellulose and lignin content) of raw switchgrass. The morphological analysis of pretreated switchgrass in our previous study (Sarkar et al., 2014) confirmed the destruction of fibrous structure by shear force during the extrusion process leading to the exposure of interior structure. These structural changes may have affected the micro-scale heat and mass transfers during the pyrolysis, e.g. decomposition may initiate from the interior portion of the particles rather than propagate from the outer surface, thereby leading to the variation in the pyrolysis products.

The effect of pyrolysis temperature on the pyrolysis products obtained from densified switchgrass was very different from those obtained from torrefied switchgrass. As seen in Figs. 1–3, the anhydrous sugars contents obtained from densified switchgrass and switchgrass pretreated with combined torrefaction and densification increased significantly from 2.41, 8.40 area%, respectively, at the pyrolysis temperature of 500 °C to 8.89 and 12.10 area%, respectively, at the pyrolysis temperature of 700 °C. However, anhydrous sugars obtained from switchgrass torrefied at 230 and 270 °C decreased significantly as the pyrolysis temperature increased from 500 to 700 °C. Furans obtained from densified switchgrass decreased with increase in pyrolysis temperature (25.66, 20.25 and 21.46 area% at 500, 600 and 700 °C, respectively). On the contrary, furans obtained from switchgrass torrefied at 230 °C increased consistently with pyrolysis temperature (16.99–20.23 area% at pyrolysis temperature of 500–700 °C, respectively). Phenols obtained from densified switchgrass increased from 4.88 to 16.12 area% first as the pyrolysis temperature increased from 500 to 600 °C, followed by a decrease to 13.50 area% at 700 °C. On contrary, phenols obtained from switchgrass torrefied at 230 °C increased consistently as the pyrolysis temperature increased (7.92–21.34 area% at 500–700 °C, respectively). Guaiacols compound obtained from densified switchgrass first decreased from 16.63 to 12.13 area% as the pyrolysis temperature increased from 500 to 600 °C, and then did not change significantly with further increase in pyrolysis temperature at 700 °C. By contrast, the guaiacols obtained from switchgrass torrefied at 230 °C decreased consistently as the pyrolysis temperature increased (14.80–9.80 area% at 500–700 °C, respectively). The aromatic compounds obtained from switchgrass pretreated with either torrefaction or densification increased consistently as the pyrolysis temperature increased. The highest aromatics yield was 17.70 area% obtained from switchgrass torrefied at 270 °C at pyrolysis temperature of 700 °C.

4. Conclusions

The effects of torrefaction and densification on pyrolysis products os switchgrass were investigated. Contents of anhydrous sugars and phenols obtained from torrefied switchgrass were higher than those obtained from raw switchgrass. The contents of anhydrous sugars and phenols also increased as the temperature of torrefaction increased. Densification enhanced the depolymerization of cellulose and hemicellulose thus promoted the production of small molecules such as furans, ketones and acids. Higher pyrolysis temperature favored decomposition of lignin and anhydrous sugars, resulting in increased yields of phenols, aromatics and furans.

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Appendix A. Supplementary data

A conversion pathway of lignin catalytic fast pyrolysis (adapted with modification from Mullen and Boateng, 2010) is provided as supplementary material. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.biortech.2014.10.032.

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